# Strategy for improving photocatalytic ozonation activity of g-C$_3$N$_4$ by halogen doping for water purification

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### ABSTRACT

Feasibility of improving photocatalytic ozonation (PCO) activity of g-C$_3$N$_4$ (CN) by doping halogen (F, Cl, Br and I) was evaluated from the aspect of O$_3$/O$_2$ mass transfer and photogenerated electron (e$^-$) and hole (h$^+$) recombination. All halogen-CN had better activity (F-CN>I-CN>Cl-CN>Br-CN) for degrading ATZ than that of CN. Experimental and theoretical simulations results showed that doping halogen made the electron unevenly distributed and formed hydrophobic sites on CN, narrowed E$_g$ of CN and enlarged e$^-$ migration space. The above properties were favorable for enhancing mass transfer of O$_3$/O$_2$ and suppressed e$^-$-h$^+$ recombination. Besides, they either upshifted CB (C-I) or downshifted VB (C-F, C-Cl) to enhance the oxidation function of •OH or h$^+$. One-electron reduction (high e$^-$ utilization) of O$_3$ was weakened and three-electron reduction (low e$^-$ utilization) of O$_2$ was enhanced with decrease of halogen electronegativity. This work provided insights into catalyst design for PCO process.

## 1. Introduction

The existence of trace pollutants had posed great threatens to water quality. Atrazine (ATZ) was widely used as herbicide [1]. It had many adverse impacts on both environment and humankinds. For instance, it was considered as an endocrine disruptor and would cause the feminization of frog [2,3]. Because of its stable covalent structure, ATZ was inert to conventional water treatment technology [4]. The cost-effective treatment was urgently needed.

Ozonation was the common water purification technology, which was normally employed for decolor, deodorize and decontamination [5]. However, restrained by the limited oxidation potential of O$_3$ (2.07 eV), sole ozonation was low in removing pollutants like ATZ [6]. At the same time, it would always generate toxic by-products, such as bromate. Moreover, the O$_3$ utility rate was also not high [7–9]. Various kinds of active solids were introduced to transform O$_3$ into secondary radicals with greater oxidation potential (mainly •OH, 2.78 eV) [10,11]. The above multi-phase system was known as catalytic ozonation, which was characterized for the higher O$_3$ utility rate, the greater pollutants removal and the less toxic by-products generation [12–14]. The active sites of ozonation catalyst were often related with electron-rich region like Lewis sites, oxygen vacancies, N vacancies, low valence metals [7].

For the reductive activation of O$_3$, electron was gradually migrated from catalysts to their surface bonded O$_3$. Unfortunately, the continuous loss of inherent electrons would inactivate catalysts (activators for more precisely) if no additional electron was supplied. Moreover, heterogeneous catalytic ozonation also suffered from the dilemmas of limited mass transfer of reactants, and the secondary pollution caused by leached metal [5]. In this regard, the combination of ozonation with photocatalysis, which was termed as photocatalytic ozonation (PCO), could be emerged as the cost-effective alternative for activating O$_3$ [15]. Similar with persulfate mediated photocatalysis process, during PCO process, O$_3$ also acted photogenerated electrons (e$^-$) consumer and trapped e$^-$ immediately, which formed •OH simultaneously [16]. Because the involved electron was excited by light, the inactivation of catalyst due to the loss of their inherit electron could be overcome. Moreover, due to the consumption of e$^-$ by O$_3$, photogenerated holes (h$^+$) had enough time to oxidize pollutants or transform H$_2$O into •OH when its oxidation potential was higher than that of H$_2$O/•OH [17]. Therefore, PCO could be regarded as cost-effective water treatment process both for overcoming the mentioned limitations of ozonation and h$^+$-e$^-$ recombination of photocatalysis. To this end, efficient semiconductor catalysts were required to provide abundant e$^-$ for O$_3$'s activation process. For instance, catalysts with ultraviolet light response,

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such as Fe-CeO$_{2-\sigma}$, GO-TiO$_2$ etc, were designed and employed successfully in PCO for p-chlorophenol and primidone [15,18].

Because of the fact that ultraviolet light only accounted for 5% energy of solar light, catalysts with visible light (Vis) response had bright prospects in PCO process. g-C$_3$N$_4$ (CN) was a typical kind of Vis-response semiconductor, with s-triazine ring as basic unit and conduction band (CB) potential at −1.30 eV. Since O$_3$/•O$_3^-$'s reduction potential was 1.6 eV, therefore, O$_3$ could capture and react with e$^-$ easily [19]. Cao's group had done excellent works on the application of CN in PCO process and they thought that the reduction of O$_3$ into •OH by e$^-$ followed the one-electron reduction pathway (SER,O$_3$→ • O$_3^-$/HO$_3$ • → • OH) [19–21]. But we found that there still existed some limitations for CN based PCO: (1) N atoms in the bridge site, which connected three s-triazine rings, did not involve in the composition of neither conductive band (CB) nor valence band (VB) [22]. Therefore, h$^+$-e$^-$ could only separate and migrate in a s-triazine ring; (2) Considering the predominant amount of O$_2$ over O$_3$ in sparged gas, it should be noted that the excessive O$_2$ would also consume e$^-$ via three-electron reduction pathway (TER, O$_2$→ • O$_2^-$/HO$_2$ • →H$_2$O$_2$→ • OH), which was suggested as low utilization of e$^-$ [19]. Moreover, hydrophilic CN had no selectivity towards O$_3$'s mass transfer, great deal of O$_3$ was not utilized [23]. The existing methods for improving behavior of catalysts were precious metal modification or building heterojunction [24,25]. These methods could only separate h$^+$-e$^-$ in a limited area on catalysts, the mentioned drawbacks were not well solved. Hence, we thought that: was it feasible to boost O$_3$'s mass transfer and enrich its surface concentration on CN

for the convenient consumption of e$^-$ and generation of •OH?

Taking the hydrophobicity and electrophilicity of O$_3$ into consideration, we tried to build hydrophobic sites and make the electron unevenly distributed on CN by doping halogen (F, Cl, Br, I) into its framework. O$_3$ had high affinity toward hydrophobic areas and sites with rich electron. Chen et al. had found that F would replace Si-OH on MCM-41 and form the hydrophobic and electron withdrawing Si-F group to accelerate mass transfer of O$_3$ [26]. Hence, the hydrophobic carbon-halogen bond could also enhance the mass transfer of O$_3$, which accelerated SER reaction and improved utilization rate of O$_3$ and e$^-$. Meanwhile, because of the difference in electronegativity, the introduction of halogens could redistribute the electron on CN. Therefore, h$^+$-e$^-$ could transfer between s-triazine rings, which reduced their recombination rate. In order to verify our proposal, ATZ was selected as model pollutant to explore the activity of halogen-CN in PCO process. Systematic experiments, characterizations and theoretical results were used to explore the reaction mechanism.

## 2. Experimental sections

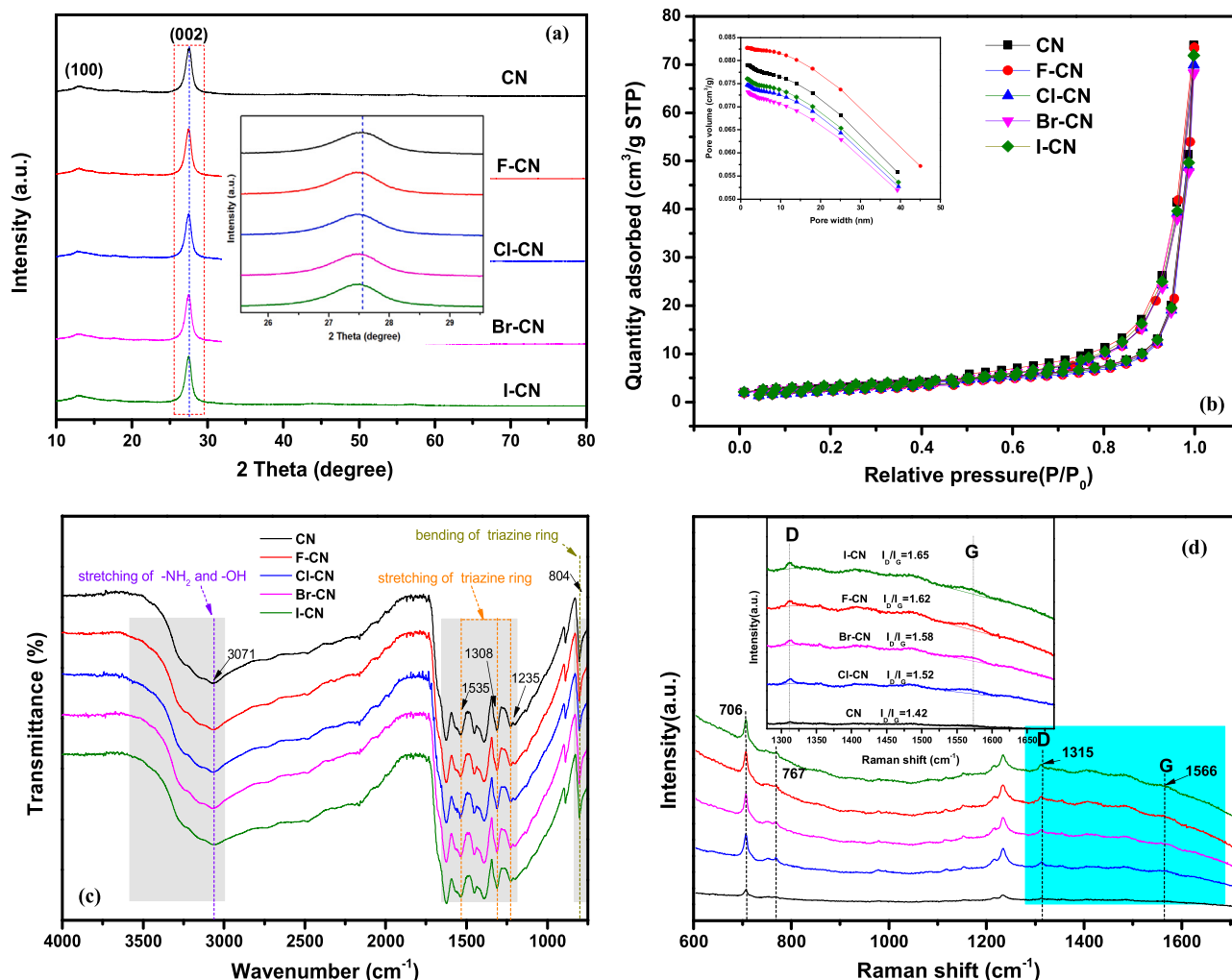Chemical regents, catalyst preparation, analysis and calculation methods were enclosed in Supplementary materials.



**Fig. 1.** (a) XRD, (b) N$_2$ adsorption-desorption isotherm, (c) FTIR and (d) Raman spectra of different CN.

## 3. Results and discussions

### 3.1. Characterizations of catalysts

The successful preparation of catalysts was confirmed by XRD. As exhibited in Fig. 1(a), there were a small peak at 2theta = ∼ 13.1° and a strong peak at 2theta = ∼ 27.6° for all CN based samples, which were corresponding to JCPDS Card 87-1526. Generally, the peak at ∼ 13. 1° was referred as (100) plane formed by s-triazine unit and the peak at ∼ 27.6° was the (002) plane resulted from the accumulation of aromatic fragments [27]. Compared with pure CN, the doping of F, Cl, Br and I atom shifted the (002) plane to the lower angle (∼ 27.4°), which suggested the increase of cell unit or inter planar spacing. Taking the atomic radius of F (0.68 nm), Cl (0.99 nm), Br (1.14 nm), I (1.46 nm) and N (0.74 nm) into consideration, Cl, Br and I should enlarge cell unit of CN because of their greater atomic radius than that of N. The doping of F ought to shift the (002) plane to the larger angle, but $NH_3$ (formed during hydrothermal of ammonium halide) would depart CN layer and increase inter planar spacing, which remedied the shrinking of cell unit. Morphologies of CN before and after halogen doping were recorded by TEM (Fig. S1). All samples presented the interlayer stacked structure and no difference was found, which indicated that the incorporation of halogen atoms did not damage CN's framework.

$N_2$ adsorption-desorption isotherms and FTIR results also verified that there was no obvious structural damage during modification. All $N_2$ adsorption-desorption isotherms were type III (Fig. 1(b)). As shown in Table 1, $S_{BET}$ were measured as 11.6, 10.9, 11.4, 11.6 and 12.3 $m^2/g$ for CN, F, Cl, Br and I-CN, respectively. $S_{BET}$ discrepancies were within the error range, suggesting that the doping of halogens had no improvement on $S_{BET}$. As shown in Fig. 1(c), the bending mode of s-triazine ring had a peak at ∼ 804 $cm^{-1}$ and the stretching vibration at ∼ 1200–1650 $cm^{-1}$ [28,29]. The signal between 3000 and 3600 $cm^{-1}$ was referred as the stretching vibration of -$NH_2$ and –OH [30]. Because of the detection limitation of FTIR, no peak of C-X (X = F, Cl, Br, I) bond was detected for halogen-CN. All samples presented the similar FTIR spectra, which further confirmed that the structure of CN was not damaged after doping with halogens by hydrothermal treatment.

Raman spectroscopy and XPS were also carried out. As depicted in Fig. 1(d), two characteristic peaks at 706 and 767 $cm^{-1}$ were found for all CN samples. The board peak at the range of 1000–2000 $cm^{-1}$ was resulted from the fluorescence absorption of conjugated layered structure. D band and G band could be observed at 1315 $cm^{-1}$ and 1566 $cm^{-1}$, respectively. Generally, $I_D/I_G$ ratio was used as index of C defects [31]. $I_D/I_G$ ratio increased after halogen doping, which suggested that halogens would disorder the structure and enrich the surface defect. More information on C—X bond was illustrated by XPS. Besides C and N elements, halogen atoms were also detected in the XPS survey with F 1 s centering at ∼ 698.0 eV, Cl 2p centering at ∼ 197.5 eV, Br 3d centering at ∼ 69.2 eV, I 3d centering at ∼620.0 eV (shown in Fig. S2). And the exact incorporated amount halogen was 0.61% for F-CN, 0.13% Cl-CN, 0.10% Br-CN and 0.07% I-CN (Table S1). As shown in Fig. 2(a), C1s of CN was deconvoluted into superficial amorphous C (C-C/C═C, ∼284.8 eV), C-O of surface absorbed-$H_2O$ (∼286.1 eV) and the sp$^2$ hybridization in s-triazine units (N—C═N, ∼ 288.5 eV) [32]. After doping with halogens, four new peaks at 289.5, 286.3, 285.8 and 285.7 eV, which were corresponded to C-F, C-Cl, C-Br and C—I bond, occurred for

F-CN, Cl-CN, Br-CN and I-CN, respectively (Enlarged figures could be found at Fig. S3) [33,34]. Compared with that of CN, binding energy of the N-C≡N peak on F-CN became larger but it shifted to the lower binding energy for the case of Cl, Br and I-CN. As for N 1s spectrum (Fig. 2(b)), it was deconvoluted into four peaks centering at ∼ 398.8 eV (sp$^2$ hybrid N (C-N═C)), ∼ 399.6 eV (bridged N (N-(C)$_3$)), ∼401.2 eV (N—H bond), and ∼404.2 eV (π-π * excitation between stacked layers) [32]. After doping with halogens, both C-N═C and N-(C)$_3$ peaks of F-CN shifted to the larger binding energy but they shifted to the lower binding energy for Cl-CN, Br-CN and I-CN. F had the strongest electronegativity (3.98), therefore, part of the electrons on bulk CN were withdrawn by F, which led to the shift of N-C═N, C-N═C and N-(C)$_3$ peaks to the greater binding energy. With the increase of atomic number, the electronegativity of Cl (3.16), Br (2.96) and I (2.66) decreased. Therefore, the inherent electron of Cl, Br and I would migrate to bulk CN, which resulted in the shift of characteristic peaks to the lower binding energy [22]. N-(C)$_3$% and C—N═C% were also calculated to investigate the incorporation sites of halogens. N-(C)$_3$% and C—N═C% was 55.2% and 33.1% for CN. N-(C)$_3$% decreased to 26.8% after doping by F, which verified the replacement of N with F. Similarly, C—N═C% decreased to 41.3%, 48.9% and 43.1% after doping with Cl, Br and I, respectively. The decline of C—N═C% indicated the replacement of edge N by Cl, Br and I. Two peaks with chemical shift of ∼150.0 and ∼161.1 ppm were observed in $^{13}C$ NMR spectrum (Fig. 2(c)). The chemical shift was in the scope of ab initio calculations results, which verified the heptazine unit in CN polymer (Fig. 2(e)) [35]. The peak at ∼ 150.0 ppm was attributed to tri-coordinate carbon ($C_i$) within the s-triazine ring and the chemical shift of ∼ 161.1 ppm was the tri-coordinate ($C_e$) carbon connected to another s-triazine ring [36]. As for $^{15}N$ NMR spectrum (Fig. 2(d)), four characteristic peaks were observed at chemical shift of ∼ 113.8, ∼ 136.0, ∼ 162.9 and ∼ 194.6 ppm, which were attributed to terminal N ($N_{t2H}$), bridge N ($N_{tH}$), central N ($N_i$) and edge N ($N_c$) [35,37]. Intensity of central N ($N_i$) and edge N ($N_c$) for F, Cl, Br and I-CN decreased when compared with that of CN, which suggested the potential substitution of central N and edge N with F/Cl/Br/I atom. NMR results were consistent with XPS results and they all confirmed the successful preparation of CN and halogen-CN.

DFT calculation was performed to further investigate doping sites of halogen and their influence on lattices parameters. The in-plane lattice constant of the optimized structure of monolayer CN was 7.12 Å, which was consistent with reported literatures [22]. As shown in Fig. 3(a), there were three types of N atoms (named as N1, N2 and N3) and two types of C atoms (named as C1 and C2) in CN. N1—C2, C2—N2, N2—C1 and C1—N3's bond lengths were 1.39, 1.33, 1.33 and 1.47 Å, respectively. The most favorable site for halogens atoms doping were investigated by calculating their formation energy (Text S1). According to the definition of formation energy, the substitutable positions for halogens were the site with the smallest formation energy.

As depicted in Fig. 3(b–e) and Table 2, F was more likely to replace N1 (namely central N) whereas Cl, Br, and I were more likely to incorporate at N2 (namely edge N) sites both for C and N rich environment. Lengths of C1-N3, C2-N2, N2-C1 and N1-C2 were shorten after halogens doping while the C-X (X=F, Cl, Br and I) were enlarged when compared with C-N of CN (Table S2).

### 3.2. Photocatalytic ozonation processes

Fig. 4(a) showed that after the doping of halogens into CN, PCO efficiencies toward ATZ were enhanced in different degrees. ATZ removals in 15 min and the first order kinetic rate constants were in the order of: $O_3$/Vis/F-CN (66.5%, 0.0695 $min^{-1}$) > $O_3$/Vis/I-CN (61.2%, 0.0637 $min^{-1}$) > $O_3$/Vis/Cl-CN (57.1%, 0.0573 $min^{-1}$) > $O_3$/Vis/Br-CN (49.8%, 0.046 $min^{-1}$) > $O_3$/Vis/CN (44.0%, 0.0392 $min^{-1}$). Taking the exact incorporated amount of halogen into consideration, I-CN still had the better activity than those of Cl, Br-CN though they had the similar atomic percentage. Moreover, their activity order during PCO

**Table 1**
Textual properties of CN and halogen-CN.

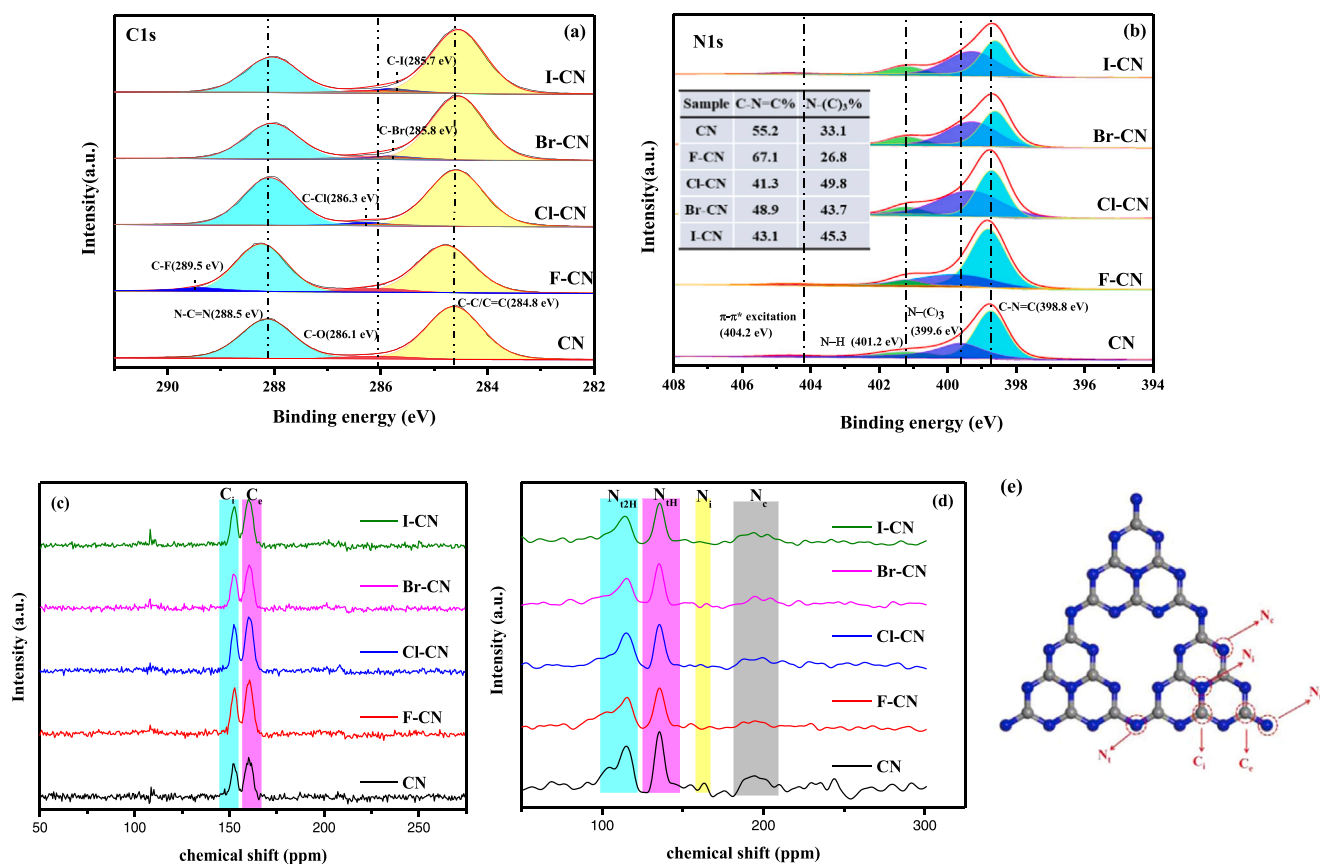| Catalysts | $S_{BET}$ ($m^2/g$) | Pore size (nm) | Pore volume ($cm^3/g$) |
|---|---|---|---|
| CN | 11.6 | 10.9 | 0.032 |
| F-CN | 10.9 | 11.1 | 0.030 |
| Cl-CN | 11.5 | 10.6 | 0.030 |
| Br-CN | 11.6 | 10.3 | 0.029 |
| I-CN | 12.3 | 10.1 | 0.031 |

**Fig. 2.** (a) C 1s pattern, (b) N 1s pattern, (c) $^{13}$C NMR, (d) $^{15}$N NMR of different CN and (e) basic unit of CN.



**Fig. 3.** Optimized structure of (a) CN, (b) F-CN, (c) Cl-CN, (d) Br-CN and (e) I-CN.

**Table 2**
Formation energy of halogens doping.

| Doping sites | F | | Cl | | Br | | I | |
|---|---|---|---|---|---|---|---|---|
| | C-rich | N-rich | C-rich | N-rich | C-rich | N-rich | C-rich | N-rich |
| C1 | 5.80 | 6.45 | 6.49 | 7.14 | 7.58 | 8.23 | 8.84 | 9.49 |
| C2 | 2.74 | 3.39 | 5.77 | 6.42 | 7.72 | 8.37 | 5.13 | 5.78 |
| N1 | **1.53** | **1.05** | 6.80 | 6.31 | 9.44 | 8.95 | 11.71 | 11.23 |
| N2 | 1.96 | 1.48 | **3.72** | **3.23** | **4.43** | **3.94** | **4.84** | **4.35** |
| N3 | 5.48 | 5.00 | 8.31 | 7.82 | 10.15 | 9.66 | 12.67 | 12.18 |

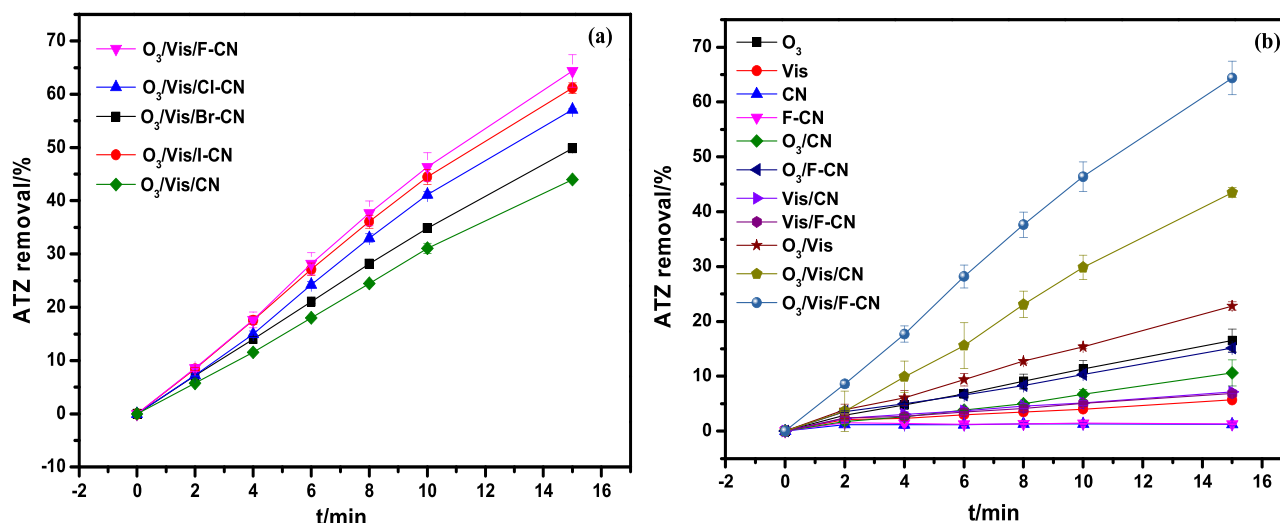**Fig. 4.** (a) Influence of halogen type on ATZ removal; (b) Systematically comparison of ATZ degradation by $O_3$/Vis/F-CN process; Reaction parameters: dosage of catalyst: 0.2 g/L; ATZ concentration: 10 mg/L; volume: 700 mL; temperature: 25 °C.

was also inconsistent with order of halogen incorporated amounts. For the deeper exploration of the function of halogens in CN, the more detailed comparisons were made among $O_3$, Vis, $O_3$/Vis, Vis/catalysts, $O_3$/catalysts, $O_3$/Vis/catalysts. Taking $O_3$/Vis/F-CN system as example (shown in Fig. 4(b)), no ATZ adsorptions were found by both CN and F-CN. Sole ozonation, Vis/CN and Vis/F-CN were low efficiency in degrading ATZ, with only 14.9%, 6.9% and 7.1% ATZ removals were obtained. The combinations of $O_3$ with CN or F-CN were also not ideal. But ATZ removal in $O_3$/F-CN (15.1%) was greater than that of $O_3$/CN (10.0%). This increase was due to generation of greater amount of C=O groups during the modification process, which was favorable for activating $O_3$ [38]. The most remarkable improvement of ATZ degradation was observed after coupling ozonation with Vis/CN or Vis/F-CN process. About 44.0% removal rates were achieved in $O_3$/Vis/CN process and it further boosted to 66.5% for $O_3$/Vis/F-CN process. Influences of environmental engineering factors were also considered. As shown in Fig. S4 (a), (b), ATZ removal gradually increased with dosage of F-CN. The greatest ATZ removal was 69.5% when F-CN's dosage reached 0.4 g/L. ATZ removals were also enhanced with $O_3$ dosage. About 83.0% ATZ was removed in 15 min when $O_3$ dosage reached 60 mg/h. The above enhancements were due to the exposure of greater active sites and the existence of greater amount of $e^-$ consumer, which increased light penetration and adsorption, suppressed $h^+$-$e^-$ combination and generated greater amount of •OH. The influence of initial pH on ATZ removal was investigated. As shown in Fig. S4(c), ATZ removal in $O_3$/Vis/F-CN process increased with initial pH value, which could be attributed to the accelerated activation of $O_3$ into •OH by $OH^-$. The maximum removal efficiency was 88.9% at pH= 9. The feasibility of $O_3$/Vis/F-CN in real water was also explored. The water from Guanzhou River (Guangzhou City, Guangdong Province, China) was used as reaction medium and the water quality parameters were depicted in Table S3. Compared with the deionized water as reaction medium, ATZ removal decreased from 44.0% to 39.9% for $O_3$/Vis/CN and from 66.5% to 57.2% for $O_3$/Vis/F-CN when using Guanzhou River as reaction medium (Fig. S4 (d)). F-CN still had the greater performance over CN in real water medium. The decrease of performance could be attributed the competition for ROSs by inorganic and organic matter such as $NO_3^-$, $SO_4^{2-}$ and natural organic matters [39].

Synergy factor (η) was introduced to investigate the influence of halogen type. PCO process could be regarded as the coupling of ozonation (O) and photocatalysis (PC). After fitted with first-order-kinetic model, the reaction constant (k) was obtained and used to calculate η ($η = k_{PCO}/k_O + k_{PC}$). As shown in Table 3, η increased in the order of $O_3$/

**Table 3**
First-order-kinetic rate constant of ozonation, photocatalysis and photocatalytic ozonation.

| System | $k_O$ (min$^{-1}$) | $k_{PC}$ (min$^{-1}$) | $k_{PCO}$ (min$^{-1}$) | η |
|---|---|---|---|---|
| $O_3$/Vis/CN | 0.0119 | 0.0045 | 0.0392 | 2.38 |
| $O_3$/Vis/F-CN | 0.0119 | 0.0035 | 0.0695 | 4.52 |
| $O_3$/Vis/Cl-CN | 0.0119 | 0.0041 | 0.0573 | 3.59 |
| $O_3$/Vis/Br-CN | 0.0119 | 0.0046 | 0.0460 | 2.78 |
| $O_3$/Vis/I-CN | 0.0119 | 0.0028 | 0.0637 | 4.32 |

Vis/CN (2.38) < $O_3$/Vis/Br-CN (2.78) < $O_3$/Vis/Cl-CN (3.59) < $O_3$/Vis/I-CN (4.32) < $O_3$/Vis/F-CN (4.52). Because all CN based catalysts had the similar $S_{BET}$, therefore, the activity discrepancies could be attributed the change of chemical properties induced by halogen doping. Moreover, ATZ removals and η were not positive correlated with neither electronegativity nor incorporated amounts of investigated halogens, which suggested the existence of multiple factors for the improvement of CN's activity. The stability of halogen doped CN during PCO processes was also investigated. As shown in Fig. S5, during five times' successive use, about 5.56% decline of ATZ removal was observed for $O_3$/Vis/CN and about 4.27–8.06% in ATZ removal was found for halogen doped CN based PCO processes.

### 3.3. Reaction mechanism of photocatalytic ozonation

Basically speaking, PCO process still obeyed the rule of photocatalysis. The yields of $h^+$-$e^-$, separation of $h^+$-$e^-$, mass transfer of $O_2$/$O_3$ and their interfacial reaction with $e^-$ as well as the oxidation of pollutant by reactive species were highly influential to the efficiency of PCO.

The amount of $h^+$-$e^-$ was dependent on the band gap ($E_g$) of semiconductor. UV–Vis diffuse reflectance spectrum of different CN catalysts (Fig. 5(a)) reflected that the doping of halogen atoms would result in the blue shift of CN. Tauc curves were also employed by plotting $hν$ vs $(αhν)^{1/n}$ to study the $E_g$ of catalysts. α was the absorbance coefficient, h was the Planck constant, ν was referred to frequency. n was 1/2 for indirect semiconductor and 2 for direct semiconductor. According to reported literatures, CN was the direct semiconductor and the halogen modified CNs were belonged to indirect semiconductor [22,40]. As shown in Fig. 5(b), $E_g$ was 2.82, 2.61, 2.61, 2.61 and 2.62 eV for CN, F-CN, Cl-CN, Br-CN and I-CN, respectively. Compared with that of CN, halogen-CN had the narrower $E_g$, which indicated that they had the greater optical adsorption and the greater generation of $h^+$-$e^-$. As shown
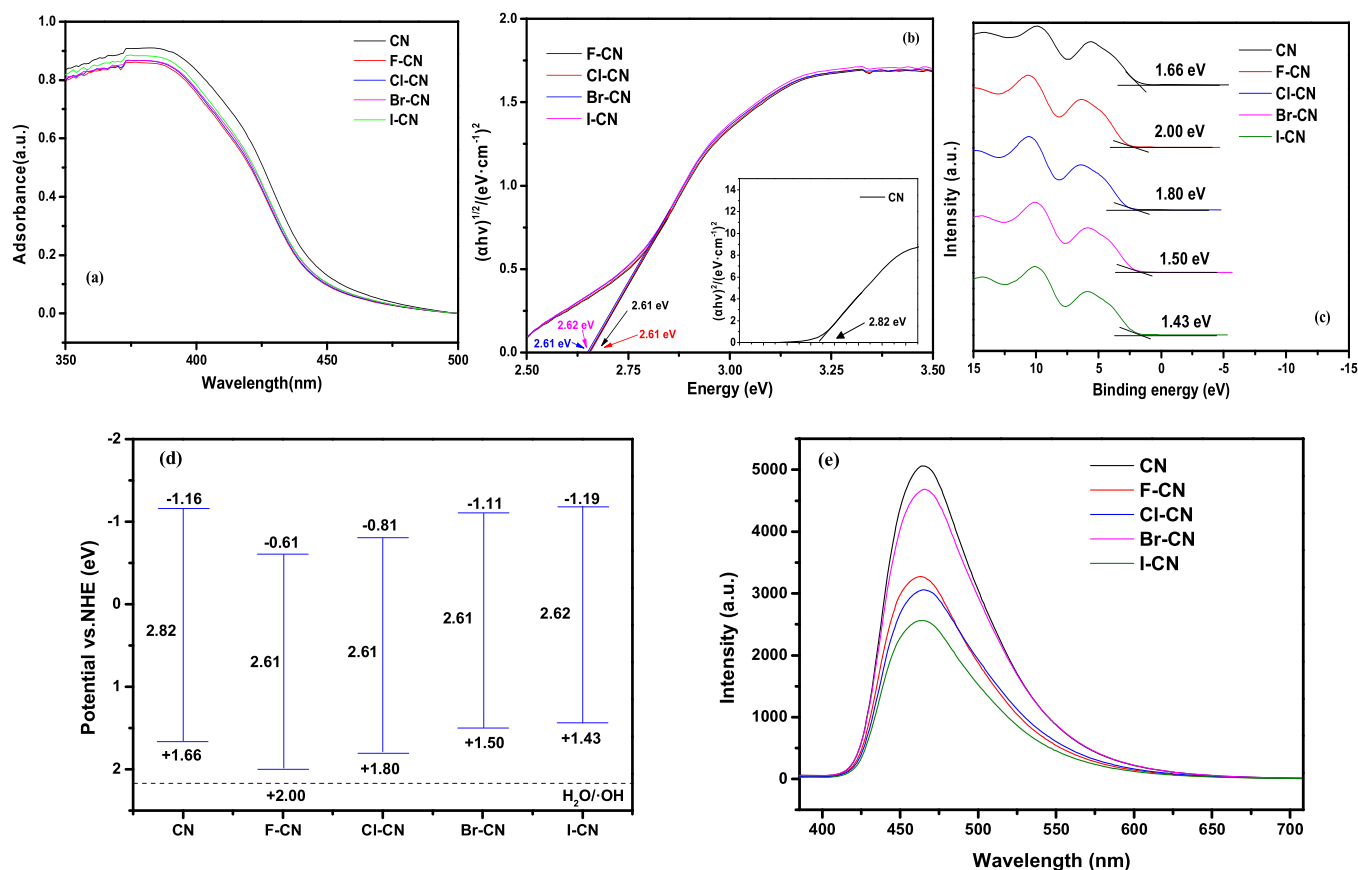
**Fig. 5.** (a) UV–vis DRS spectra; (b) Tauc plots; (c) VB XPS spectra; (d) Band structure; (e) PL spectra.

in Fig. 5(e), the fluorescence intensities (with emission wavelength at ~ 475 nm) of catalysts decreased obviously in the order of I-CN<Cl-CN<F-CN<Br-CN<CN. Generally speaking, the lower fluorescence intensity indicated the lower $h^+$-$e^-$ recombination rate [41]. Therefore, it was reasonable to infer that $e^-$ had the larger migration space on halogen-CN than that on CN (proved by HOMO and LUMO calculation in latter parts). Fig. 5(c) was the VB XPS of five kinds of CN. VB potentials were measured as 1.66, 2.00, 1.80, 1.50 and 1.43 eV for CN, F, Cl, Br and I-CN, respectively. And their CB potentials were −1.16, −0.61, −0.81, −1.11 and −1.19 eV. VB potential was related with the
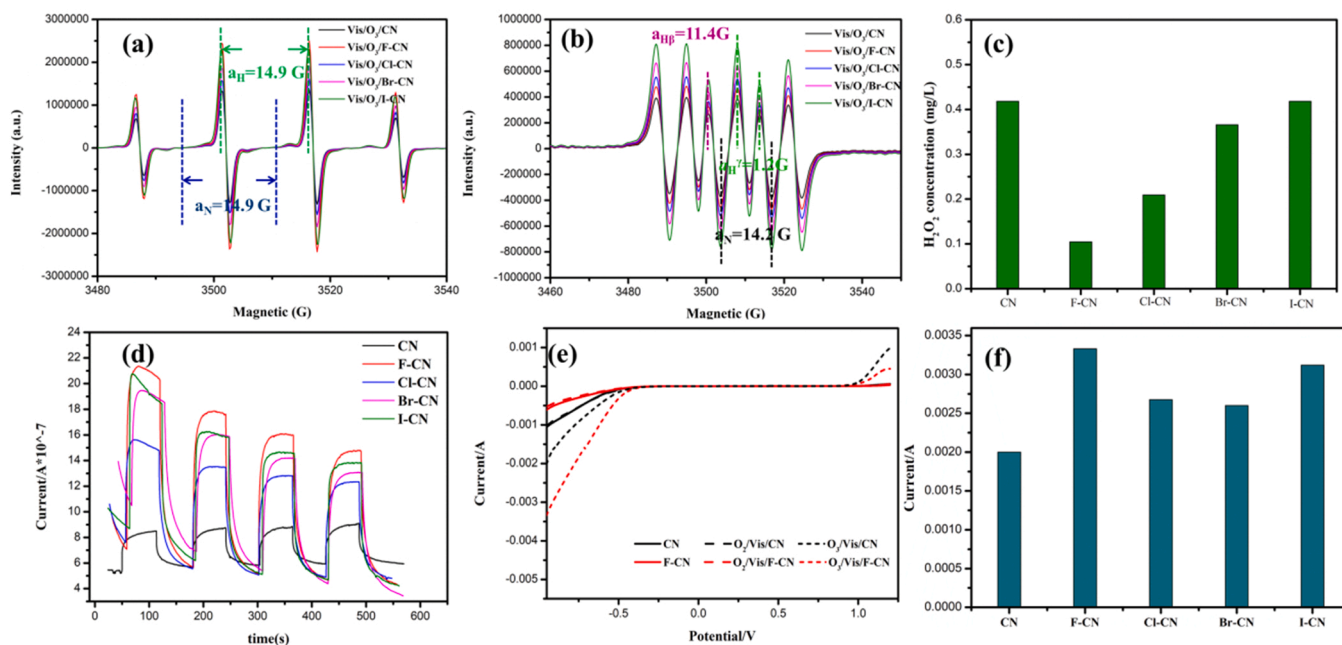


**Fig. 6.** EPR pattern of ●OH-DMPO adducts (a) and ●O$_2^-$-DMPO adducts (b), H$_2$O$_2$ generation (c), (d) photo-currents, (e) linear sweep voltammetry curve (LSV) characterization and (f) initial current of different PCO process.

oxidation capacity of $h^+$. Generally, $h^+$ could oxidize the surface absorbed $H_2O$ into $\bullet OH$ [42]. Meanwhile, it could also oxidize pollutant directly [43]. The oxidation potential of $H_2O/\bullet OH$ was 2.27 eV, which was much greater than the VB potential of CN and halogen-CN [43]. Therefore, the possibility of transforming $H_2O$ into $\bullet OH$ by $h^+$ was excluded. Hence, the role of $h^+$ in this study was mainly referred as its direct oxidation of pollutant. As for photogenerated $e^-$, its reaction with $O_2/O_3$ was effected by the reductive capacity of CB [44]. Among the investigated CN and halogen-CN, I-CN possessed the lowest CB potential, which meant that the reaction between $e^-$ with $O_2/O_3$ on I-CN was more favorable than other kinds of catalysts.

Based on the above discussions, the generation amount of $\bullet OH$, $\bullet O_2^-$ and $H_2O_2$ were recorded to interpret the reaction between $O_3/O_2$ with photogenerated $e^-$. EPR was conducted to detect $\bullet OH$ and $\bullet O_2^-$ with DMPO as trapping molecular. DMPO would react with $\bullet OH$ and generated $\bullet OH$-DMPO complex, which presented the characteristic 1:2:2:1 pattern [45]. $\bullet O_2^-$ detection was conducted in methanol solution to inhibit the interference of $\bullet OH$ and the $\bullet O_2^-$-DMPO normally exhibited sextet peaks [46]. As shown in Fig. 6(a), the $\bullet OH$-DMPO adducts (hyperfine splitting couplings were $a_N = a_H = 14.9$ G), were detected in all PCO processes and their signals were in the order of $O_3/Vis/F$-CN > $O_3/Vis/I$-CN > $O_3/Vis/Br$-CN > $O_3/Vis/Cl$-CN > $O_3/Vis/CN$. After removing dissolved $O_3$ by bubbling Ar into solution, the signal of $\bullet OH$-DMPO adducts for all CN based photolysis processes were much less than those of PCO processes, which verified the essential existence of $O_3$ for generating $\bullet OH$ (Fig. S6). During PCO process, both $O_3$ and $O_2$ could serve as $e^-$ consumer and generated $\bullet OH$ through SER or TER pathways, respectively [19]. Because of the impossibility for $h^+$ to oxidize $H_2O$ into $\bullet OH$, $\bullet OH$ should be positive correlated with CB potential. As shown in Fig. 5(d), CB potential was in the order of I-CN>Br-CN>Cl-CN>F-CN>CN. F-CN had the lowest CB position but $O_3/Vis/F$-CN process had the greatest $\bullet OH$ amounts, which indicated that other factors should be considered for generating $\bullet OH$ besides the band position of catalysts. Carbon halide bond was known as hydrophobic [47]. Hence, halogen modified CN should have the better affinity towards $O_3$ and $O_2$ than that of CN. Among the investigated halogens, F had the strongest electronegativity and the formed C-F zone would withdraw electron from the s-triazine ring and construct the zone with rich electron, which endowed F-CN with selectiveness toward electrophilic $O_3$ [48]. Eqs. (1)–(8) indicated that the theoretical $e^-$ consumption for reducing $O_3$ into $\bullet OH$ was one third of reducing $O_2$ into $\bullet OH$. Therefore, $O_3$ could utilize $e^-$ more efficiently and generate more $\bullet OH$. The inconsistent order between CB potential and $\bullet OH$ amount suggested that the enhanced mass transfer of $O_3$ could compensate for the increase of CB potential.

$$h^+ - e^- \xrightarrow{hv} h^+ + e^- \qquad (1)$$

$$O_3 + e^- \rightarrow \bullet O_3^- \qquad (2)$$

$$\bullet O_3^- + H^+ \rightarrow HO_3\bullet \qquad (3)$$

$$HO_3\bullet \rightarrow O_3 + HO\bullet \qquad (4)$$

$$O_2 + e^- \rightarrow \bullet O_2^- \qquad (5)$$

$$\bullet O_2^- + H^+ \rightarrow HO_2\bullet \qquad (6)$$

$$HO_2\bullet + H^+ + e^- \rightarrow H_2O_2 \qquad (7)$$

$$H_2O_2 + e^- \rightarrow OH^- + \bullet OH \qquad (8)$$

The sextet signals (hyperfine splitting constants of $a_N = 14.2$ G, $a_H^\beta = 11.4$ G, and $a_H^\gamma = 1.2$ G), which were characteristic for $\bullet O_2^-$-DMPO adducts, were detected for all PCO processes and their intensities were in the order of $O_3/Vis/I$-CN > $O_3/Vis/Br$-CN> $O_3/Vis/Cl$-CN > $O_3/Vis/F$-CN > $O_3/Vis/CN$ (Fig. 6(b)). As discussed in former parts, $\bullet O_2^-$ was an

important intermediate of $O_2$'s TER reaction (Eqs. (5)–(8)) [19]. Hence, the tendency of $\bullet O_2^-$ amounts in halogen-CN PCO processes suggested that the possibility of TER reaction between $e^-$ and $O_2$ increased with atomic number of halogens. As proposed in former parts, C-F groups, which endowed g-$C_3N_4$ the selective affinity towards $O_3$ by the electron-rich zone, could reduce the inefficient use of photogenerated $e^-$ by $O_2$. Therefore, $O_3/Vis/F$-CN had the smallest $\bullet O_2^-$-DMPO signal among halogen-CN processes. However, with the increase of atomic number, the electronegativity of Cl, Br and I decreased. The electron of Cl, Br and I might migrate to the bulk CN, which reduce their selectiveness towards electrophilic $O_3$ [48]. Generation of $H_2O_2$ was also detected to investigate the reaction between $O_2$ and $e^-$ (Fig. 6(c)). $H_2O_2$ was known as the important intermediate for the TER reaction of $O_2$ [19]. Therefore, the identical order of $H_2O_2$ accumulation amount with $\bullet O_2^-$-DMPO intensity also served as evidence of the TER process. The interfacial electron transfer was investigated by photocurrents and linear sweep voltammetry curve (LSV) characterizations. Fig. 6(d) depicted that all halogen-CN had the greater photocurrents than that of CN. Photocurrent was resulted from the excitation of $e^-$ by photons from VB to CB [49]. The enhancement of photocurrent could be ascribed to both the narrowing of $E_g$ and the surface polarization of halogen-CN. As proposed by Teng, the polarized internal electric field within semiconductors could accelerate the $e^-$ migration [50]. The differences of photocurrent indicated the increase of electronic polarization by doping halogens and the degree of electronic polarization was in the order of F-CN>I-CN>Br-CN>Cl-CN. LSV reflected that the introduction of $O_2$ had limited influence on the interfacial electron migration (Fig. 6(e)). The initial current of $O_2/Vis/CN$ and $O_2/Vis/F$-CN were identical to those of CN and F-CN. However, after introducing $O_3$, initial of current enhanced dramatically, which suggested that $O_3$ had the better activity with $e^-$ than $O_2$. Trend of initial currents of different CN based catalyst in PCO processes were consistent with order of intensity of $\bullet OH$-DMPO signal (Fig. 6(f)), therefore, it further indicated that F-CN and I-CN had the better $e^-$ utilization. Meanwhile, considering the potential reduction of $O_2/H_2O$ into singlet oxygen ($^1O_2$, oxidation potential was $-0.11$ eV) by $e^-$, the generation of $^1O_2$ was also recorded by EPR with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMP) as probe agent [51]. However, the 1: 1: 1 triplet signal of TEMP-$^1O_2$ was hardly found for all PCO processes (Fig. S7). The above results were consistent with Xiao's reports, which thought that $\bullet OH$ and $\bullet O_2^-$ were the major ROSs for PCO process [19].

The contributions of oxidative species to ATZ removal were also evaluated with TBA, DMSO, p-BQ, TEOA and $KBrO_3$ acting as scavengers for dissolved $\bullet OH$, surface $\bullet OH$, $\bullet O_2^-$, $h^+$ and $e^-$, respectively [52–54]. As depicted in Fig. 7, addition of most of the mentioned scavengers inhibited ATZ removal except for $KBrO_3$. The increase of ATZ removal with the co-existence of $KBrO_3$ suggested that more $e^-$ was consumed by $KBrO_3$. Therefore, the recombination $h^+$-$e^-$ was inhibited and the direct oxidation of $h^+$ was strengthened. $KBrO_3$ had the least impact on
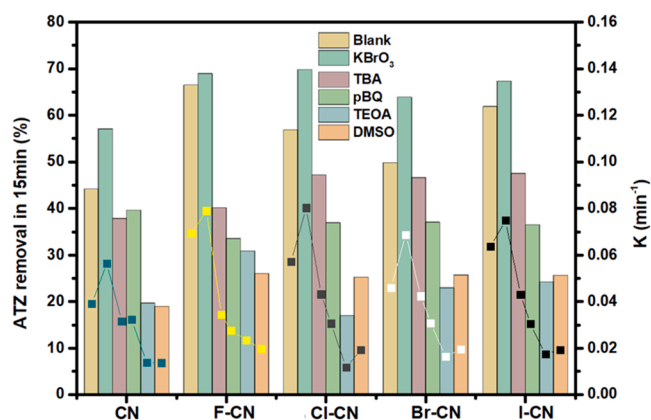


**Fig. 7.** Influence of scavenger on different PCO processes.

O$_3$/Vis/F-CN process, which indirectly reflected the better e$^-$ consumption on the surface of F-CN because of its greater affinity towards O$_3$ than that of Cl-CN, Br-CN, I-CN and CN. DMSO and TEOA had the greater inhibition rate than other kinds of scavengers for all investigated PCO processes. Therefore, it could be stated that h$^+$ and •OH (especially surface •OH) played the more important role in degrading ATZ than •O$_2^-$.

## 3.4. Theoretical calculation

DFT simulation was also employed to support the mentioned mechanism. For convenience discussion, the s-triazine rings in optimized structure were labeled as ring 1–4. Work function (Φ, Φ = E$_{Vac}$-E$_F$) was calculated to illustrate the capacity of electron diffusion from catalyst [55,56]. E$_{Vac}$ and E$_F$ were the vacuum energy level and the electrostatic potential at the Fermi level, respectively. As showed in Fig. 8, E$_F$ upshifted from −3.580 to −3.201, −2.484, −2.426 and −2.374 eV after doping CN with F, Cl, Br and I, respectively. With the increase of atomic number, the electronegativity of Cl, Br and I decrease. Therefore, the electron of halogen with greater atomic number might be transferred to CN, which upshifted the Fermi level [22]. E$_{Vac}$ were 1.208, 1.209, 1.244, 1.250 and 1.290 eV while Φ was calculated as 4.788, 4.410, 3.728, 3.676 and 3.664 eV for CN, F, Cl, Br and I-CN, respectively. The decrease of Φ with halogen doping suggested the more facility for the escaping of electron from CN surface.

LUMO and HOMO orbits of CN and halogen-CN were also investigated. As shown in Fig. 9, CN's HOMO was mainly composed by N2 atom and its LUMO was contributed by C1, C2 and N1 atom. The bridge N (N3) of CN did not participate in the HOMO and LUMO. Therefore, h$^+$-e$^-$ was primarily generated at N2 sites and then e$^-$ migrated to the adjacent atoms. Because of the insignificant contribution of N3 atom to both HOMO and LUMO, e$^-$ was limited in a single s-triazine ring, which resulted in the low separation efficiency of h$^+$-e$^-$ of CN. After doping with halogens, redistributions of HOMO and LUMO of halogen-CN were observed. Bridge N (N3) atom of halogen-CN all participated in HOMO and/or LUMO, which meant that e$^-$ could migrate in the larger space. For F-CN, F was involved in the HOMO but did not contribute to the LUMO. Under the electron-withdrawing effect of F, electron on F-containing s-

triazine ring was delocalized. C1, C2, N3 and F in the F-containing s-triazine ring (ring 1) mainly contributed to HOMO. N1, N2 and C1 of ring 4 contributed a little to HOMO. LUMO were totally distributed outside of the fluorine-containing s-triazine ring. Therefore, the oxidation reaction occurred at F-containing s-triazine and reduction reaction happened at the neighboring s-triazine (ring 2–4). For the case of Cl-CN, Br-CN and I-CN, Cl, Br and I all participated in HOMO. Besides that, C1, C2, N1, N2 on the ring 1 as well as C1, C2, N1, N2 and N3 of ring 4 also contributed to HOMO. LUMO of Cl-CN, Br-CN and I-CN were contributed by both the halogen-free s-triazine ring (major) and the halogen-containing s-triazine ring (minor). The oxidation reaction occurred at ring 1 and 4 while reduction reaction happened at ring 3 for Cl, Br and I-CN. Electron localization function (ELF) results shown that CN had the highly conjugated structure, therefore, the highly symmetrical distribution of electrons was observed (Fig. 9). Doping of halogens had different influence on electron distribution. F on F-CN could seize the surrounding electron, building an electron-rich region centering C—F bond. However, electrons of Br and I migrated to bulk because of their decline of electronegativity, generating the electron-poor zone. As for Cl-CN, the electron migration was not as obvious as other kinds of halogen and its electron distribution was not highly polarized. The above results were echoed with the XPS.

The affinity of CN based catalysts towards O$_2$/O$_3$ were illustrated by calculating adsorption energy and the greater adsorption energy suggested their greater affinity [57]. Firstly, O$_3$ was placed on C1, C2, N1, N2 and N3 sites to find the possible sites of O$_3$' adsorption on CN. Three ways of O$_3$'s adsorption were considered, namely horizontal adsorption via central oxygen atom, horizontal adsorption via edge oxygen atom and vertical adsorption via edge oxygen atom (shown in Fig. S8). As shown in Table S4, vertical adsorption of O$_3$ on N2 atom was the most favorable, with the maximum adsorption energy as −3.67 eV. The vertical adsorption model was adopted in subsequent work. O$_2$ adsorption energy at N2 of CN was −2.35 eV. During PCO process, O$_3$/O$_2$ should react with e$^-$ at CB (LUMO orbit), hence, their adsorption sites on halogen-CN were more likely at N$_2$ on ring 3 (Cl-CN, Br-CN and I-CN) and 4 (for F-CN), where were accumulated rich e$^-$ at LUMO (Fig. S9). As shown in Table 4, compared with those of CN, both O$_3$ and O$_2$ adsorption energy on halogen-CN increased, which were attributed to their
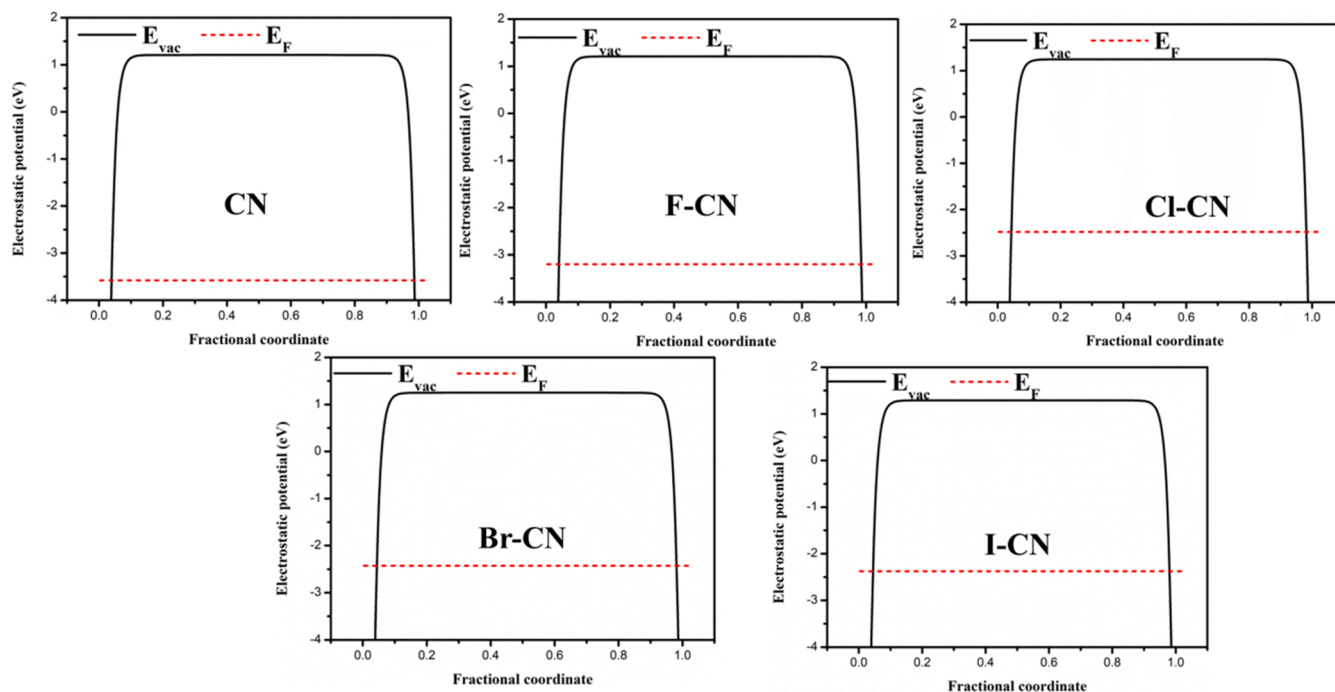


**Fig. 8.** Electrostatic potential profiles along z direction of CN and halogens-CN.
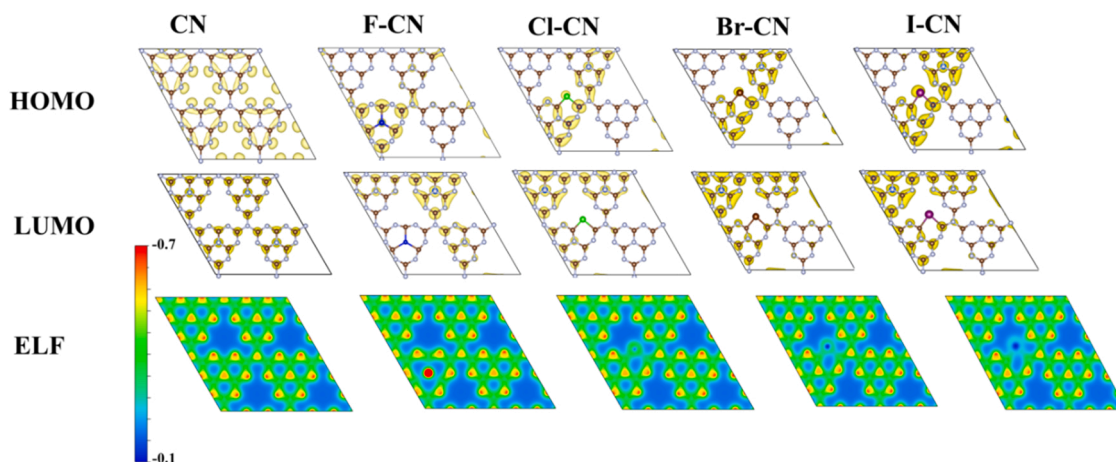
**Fig. 9.** Calculated HOMO, LUMO and electron localization function of CN and halogens-CN (isosurface value=0.05 e/Å).

**Table 4**
Adsorption energy of $O_3/O_2$ on CN and halogen-CN.

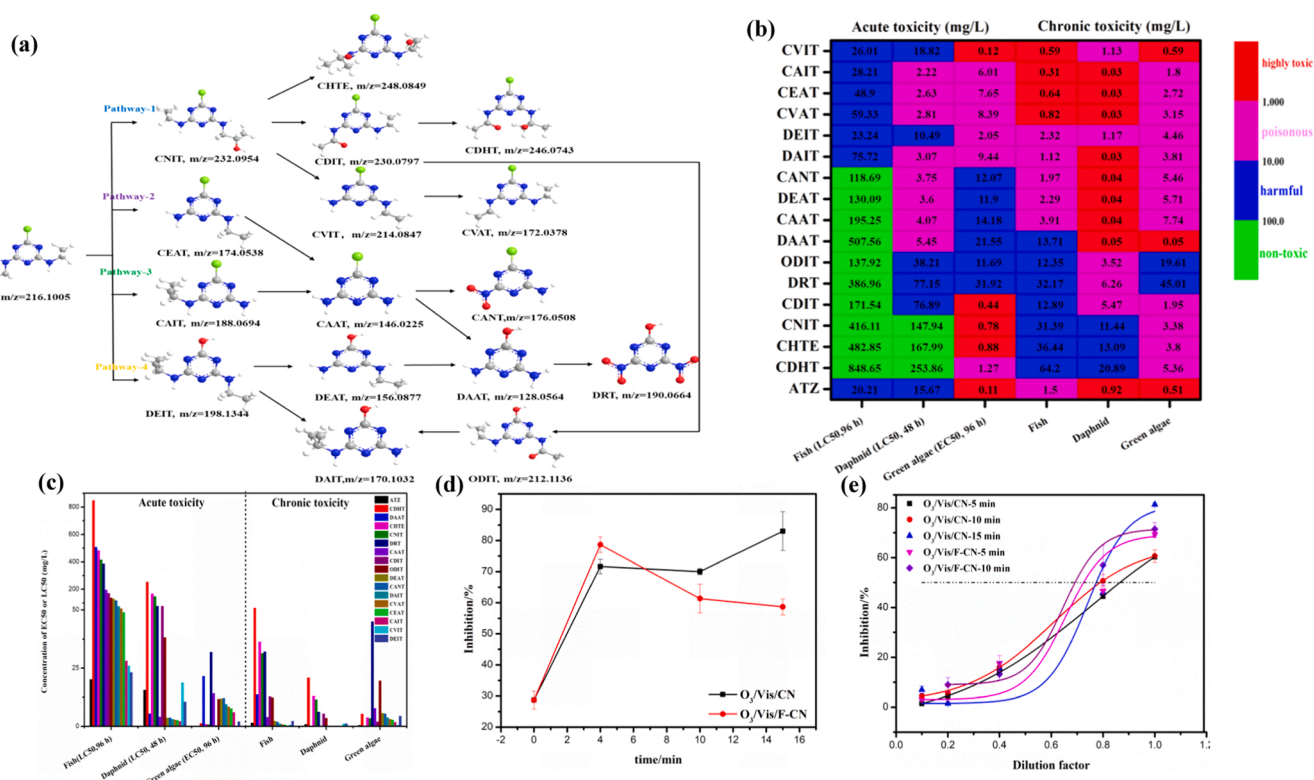| Catalysts | Adsorption energy (eV) | |
|---|---|---|
| | $O_3$ | $O_2$ |
| CN | -3.67 | -2.35 |
| F-CN | -5.53 | -4.55 |
| Cl-CN | -5.12 | -6.77 |
| Br-CN | -5.22 | -6.79 |
| I-CN | -5.48 | -6.13 |

increase of hydrophobicity. $O_3$ adsorption energies were calculated as −5.53, −5.12, −5.22, and −5.48 eV for F, Cl, Br and I-CN, respectively. $O_2$ adsorption energies were calculated as −4.55, −6.77, −6.79, and −6.13 eV for F, Cl, Br and I-CN, respectively. Hydrophobic property of CN and halogen-CN were further characterized by water contact angle (CA). As depicted in Fig. S10, CA were 23.7, 54.8, 47.5, 44.2, and 37.8° for CN, F, Cl, Br and I-CN, which reflected the increase of hydrophobicity after halogen doping. Moreover, the residual ozone concentration was measured as 4.06, 2.23, 1.00, 1.44, 1.44 and 1.67 mg/L for sole ozonation, CN and F, Cl, Br, I-CN based PCO process (Fig. S11). Compared with those of CN-PCO process, the obvious decrease of residual ozone concentration in halogen-PCO processes suggested the greater $O_3$ utility rate, which might indirectly reflect the enhanced $O_3$ mass transfer and its subsequent reaction with e⁻. The greater $O_2$ desorption signal at 300 °C were observed for halogen-CN over that of CN in $O_2$-TPD pattern, which reflected the greater $O_2$ adsorption capacity of halogen-CN over CN (Fig. S12). These results suggested that the strong adsorption of $O_3/O_2$ on F, Cl, Br and I-CN over CN facilitated the subsequent consumption of e⁻, which was favor for PCO [57]. $O_3$ adsorption energy of F-CN was the greatest among halogen-CN and it was also greater than $O_2$ adsorption energy. As proved in former parts, F on F-CN would construct electron rich zone, therefore, F-CN possessed greater affinity to electrophilic $O_3$. $O_2$ adsorption energy of Cl, Br and I-CN surpassed $O_3$ adsorption energy, which meant that they had the less selectivity toward $O_3$ when compared with F-CN.

Basing on the experimental and calculating results, common advantages of halogen doping were summarized as that they all narrowed $E_g$, enhanced $O_3/O_2$'s mass transfer and enlarged space for e⁻ migration. The differences between halogens were depicted as following: (1) C-F in F-CN could withdraw electron from CN and construct both the hydrophobic sites and electron-rich region, which endowed F-CN with the selectivity towards $O_3$ and enhanced the SER reaction to generate more ●OH. Meanwhile, C-F groups also downshifted F-CN's VB. Both h⁺ oxidation and ●OH oxidation pathways were enhanced when compared with other kinds of CN; (2) C-Cl in Cl-CN had limited influence on the

electron polarization of CN, therefore, Cl-CN had less selectiveness towards $O_3$. Due to the competition of $O_2$'s TER reaction, the utilization rate of e⁻ might not as high as that of F-CN. But, the downshift of VB of Cl-CN could strengthen the direct oxidation ability of its h⁺; (3) Br-CN had the unfavorable CB and VB potential when compared with those of CN, therefore, its greater catalytic performance than CN might be lied in its narrower $E_g$ and the greater amount of e⁻ on the surface to react with $O_2$ and $O_3$; (4) C-I in I-CN dramatically shifted its CB to upper position, which enhanced the reductive of e⁻ and the TER of $O_2$ and SER of $O_3$. The greater activity of I-CN than CN might be due to the generation of more ●OH.

*3.5. Degradation pathway of ATZ and change of toxicity*

Generation of by-products during $O_3$/Vis/F-CN was measured by LC-MS/MS for deducing ATZ degradation pathway. About 16 kinds of by-products were detected and their structures were further confirmed by secondary mass spectrometry (Table S5 and Figs. S13–31). Dealkylation, dechlorination, hydroxylation, alkylic oxidation, alkylic hydroxylation and olefination were main reactions during ATZ oxidation, which were also summarized by reported literatures [58,59]. Basing on the detected components, four possible degradation pathways were deduced and depicted in Fig. 10(a). Pathway 1 and 4 were dominated by ●OH oxidation. In pathway 1, DEX was first attack by ●OH and one side chain or both side chains of ATZ were hydroxylated, which then generated CNIT and CHTE. Then CNIT was served as precursor of CDIT via the alkylic oxidation and finally generated CDHT after the further oxidation by ●OH. Meanwhile, CVIT also formed from the olefination of CNIT. CVAT was obtained after CVIT's dealkylation. In pathway 4, ●OH attack Cl group directly and generated the hydroxylated products, namely DEIT. The step by step dechlorination was happened on both sides' chains of DEIT, generating DEAT, DAIT and DAAT. Because amino groups of DAAT were reductive, DAAT was easily oxidized to DRT accompanying with oxidation of –$NH_2$ to –$NO_2$ groups. As for pathway 2 and 3, it might be dominated by h⁺ and ●$O_2^-$. Due to their strong electronegativity, N atoms on both side chains were electron-rich and were likely to be oxidized by h⁺. Therefore, alkyl groups of ATZ were eliminated progressively to form CEAT, CAIT and CAAT. As proposed by Ye, during the dealkylation of ATZ to CEAT and CAIT, carbon-center radicals were generated because of the H extraction on the α-C next to N. The carbon-center radicals were consequently oxidized by ●$O_2^-$, which finally generated CAAT [60]. However, because of the lack of powerful equipment, the above hypothesis could only be proved by detecting the corresponding product. After that, one of CAAT's amino groups was oxidized, generating CANT. Hydroxylation and dehalogenation were also likely to happen for CAAT, and generated DAAT.

Fig. 10. (a) Proposed degradation pathway, (b-c) predicted acute and chronic toxicity of by-products, (d-e) acute toxicity of by-products on photobacterium luminescens.

ECOSAR was employed to explore the toxicity of intermediates (both acute and chronic). By referring to the LC50, EC50 and ChV values, their toxicity could be divided into: highly toxic (<1.0 mg/L), toxic (1.0–10.0 mg/L), harmful (10.0–100.0 mg/L) and harmless (>100.0 mg/L) [61]. As exhibited in Fig. 10(b-c), for the case of acute toxicity, ATZ was highly toxic to green algae but only harmful to fish and daphnid. For the case of chronic toxicity, ATZ was poisonous to fish but highly toxic for both daphnid and green algae. ATZ and its intermediates had the more significant impact on daphnid and green algae than that on fish. After the degradation, toxicity of intermediates varied with each other depending on testing species. LC50 towards fish of all intermediates increased when compared with that of ATZ during the acute toxicity test. 62.5% of intermediates were non-toxic and 37.5% of intermediates were still harmful to fish. As for chronic toxicity to fish, 43.8% of intermediates were harmful, 33.3% of intermediates were poisonous while the rested 25.0% were highly toxic. When choosing daphnid as testing species, non-toxic, harmful and poisonous intermediates accounted for 18.8%, 31.2% and 50.0% during acute toxicity test. But harmful, poisonous and highly toxic species accounted for 18.8%, 31.2% and 50.0% during chronic toxicity test. ATZ and its intermediates had the greatest impact on green algae. Though the increase of EC50 value on algae, 4 kinds of ATZ-derivatives were still high toxic, 6 kinds of the intermediates were poisonous and 6 kinds of intermediates were harmful. As for the chronic toxicity test, DAAT and CVIT were found highly toxic, DRT and ODIT were harmful, and the remaining 12 kinds of derivatives were all poisonous to algae. For summarizing the above results, intermediates in pathway 1 and 4 were less risk than those in pathway 2 and 3. The mixed acute toxicity of intermediates during $O_3$/Vis/CN and $O_3$/Vis/F-CN were tested with photobacterium luminescens as test organism. As shown in Fig. 10(d-e), the inhibition rate of ATZ towards photobacterium luminescens was 28.7% and samples in both $O_3$/Vis/CN and $O_3$/Vis/F-CN processes had the much greater inhibition rates, which suggested the greater toxicity of intermediates. In $O_3$/Vis/CN process, the toxicity of intermediates

gradually increased with degradation time. But it had an initial increase and then decreased in $O_3$/Vis/F-CN process. The toxicity of intermediates in $O_3$/Vis/F-CN was less than that in $O_3$/Vis/CN process except in the first 5 min. The EC50 value in both processes shifted to the smaller dilution factor with the proceeding of degradation and the toxic of by-products in $O_3$/Vis/F-CN was much smaller than those of $O_3$/Vis/CN. Though the obvious advantage of F-CN over CN, the completely detoxification of ATZ required more attentions in further study.

## 4. Conclusions

Halogen incorporated CN (F, Cl, Br and I-CN) were prepared to accelerate ATZ degradation during photocatalytic ozonation process. All halogen-CN had the better activity than CN and their activity was in the order of F-CN> I-CN>Cl-CN>Br-CN>CN. C-halogen bond could narrow $E_g$, enhance mass transfer of $O_3$ and/or $O_2$ and redistribute the ingredient of HOMO and LUMO to provide the larger space for $e^-$ migration. Besides the above advantages, they could also either upshift CB (C-I) or downshift VB (C-F and C-Cl) to enhance $h^+$ direct oxidation and •OH's indirect oxidation. $h^+$ and surface •OH played the major role for degrading ATZ in all CN assisted photocatalytic ozonation processes. Basing on the LC-MS/MS results, 16 kinds of by-products were detected and 4 degradation pathways were deduced. This study could serve as guiding for designing cost-effective catalyst for photocatalytic ozonation process.

## CRediT authorship contribution statement

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2022.121133.

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